

Operator equality on entropy production in quantum Markovian master equations

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(Dated: October 23, 2012)

An operator equality on the entropy production for general quantum Markovian master equations is derived without resorting quantum stochastic trajectory and priori quantum definition of entropy production. We find that, the equality can be still interpreted as a consequence of time-reversal asymmetry of the nonequilibrium processes of the systems. In contrast with the classical case, however, the first order expansion of the equality does not directly related to the mean entropy production, which arises from noncommute property of operators in quantum physics.

PACS numbers: 05.70.Ln, 05.30.-d

Introduction Irreversible processes can be seen almost everywhere in nature. Imaging that a process of an object falling into water starts from a static state and ends with some position and velocity after a finite time interval. However, if one wants to reverse the process by simply reversing the object's velocity from the ending position, the object never returns back its initial state after the same time interval. This phenomenon obviously arises from energy dissipation as heat due to friction between the object and its reservoir. In modern thermodynamics, irreversible process is always related to nonnegative entropy production [1, 2], or it is a manifestation of the second law of thermodynamics. Although the law has been rigidly established in macroscopic systems, in the past few decades, interest in the entropy production or dissipated work in small nonequilibrium systems has grown intensively due to the finding of various fluctuation theorems or relations [3–12]. These remarkable relations greatly deepen our understanding about the second law of thermodynamics and nonequilibrium physics of small systems. With the fluctuation relations clarified in the classical systems, recently, we may see an trend of extending the relations into quantum systems [13–24].

In this work, we present an *operator version* for the entropy production equality in nonequilibrium systems that can be described by quantum Markovian master equations. Because Markovian description implies that the time change of external sources does not affect reservoirs and is very slowly in comparison with reservoir's relaxation time [25], we are not intended to state that the equality obtained here holds even if the system is driven very far from equilibrium, e.g., like the entropy production equality derived by Deffer and Lutz [22] using the sophisticated two-point energy measurement statistics [17, 20]. However, we think that the price is worthwhile paying, since we can derive an exact operator equality on the entropy production. Although there have existed various quantum fluctuation relations in the literature, to our knowledge, very few of them are in operator form [23, 24].

Time-reversal of system We concern about the irreversible process of an open quantum Markovian system L_t during a time interval $(0, T)$. The equation of motion for the system's density operator $\rho(t)$ is then

$$\partial_t \rho(t) = L_t \rho(t) = L_t^{\text{irr}} \rho(t) + L_t^{\text{rev}} \rho(t), \quad (1)$$

where

$$L_t^{\text{rev}} \rho(t) = -i[H_t, \rho(t)], \quad (2)$$

H_t is free Hamiltonian of the system, and L_t^{irr} represents a dissipative term due to the interaction of the system with a heat reservoir and it has a general form [26–29]

$$L_t^{\text{irr}} \rho(t) = \frac{1}{2} \sum_j [V_j, \rho(t) V_j^\dagger] + [V_j \rho(t), V_j^\dagger]. \quad (3)$$

Here we use the subscripts t to indicate their possible time-dependence except V_j and V_j^\dagger for the simplicity in notation. We define an alternative quantum Markovian system \tilde{L}_s as a time-reversal of the system (1), if its density operator $\tilde{\rho}(s)$ satisfies a master equation of

$$\partial_s \tilde{\rho}(s) = \tilde{L}_s \tilde{\rho}(s) = \tilde{L}_s^{\text{rev}} \tilde{\rho}(s) + \tilde{L}_s^{\text{irr}} \tilde{\rho}(s), \quad (4)$$

and

$$\tilde{L}_s^{\text{rev}} A = -\Theta L_{t'}^{\text{rev}} [\Theta A \Theta^{-1}] \Theta^{-1}, \quad (5)$$

$$\tilde{L}_s^{\text{irr}} A = \Theta L_{t'}^{\text{irr}} [\Theta A \Theta^{-1}] \Theta^{-1}, \quad (6)$$

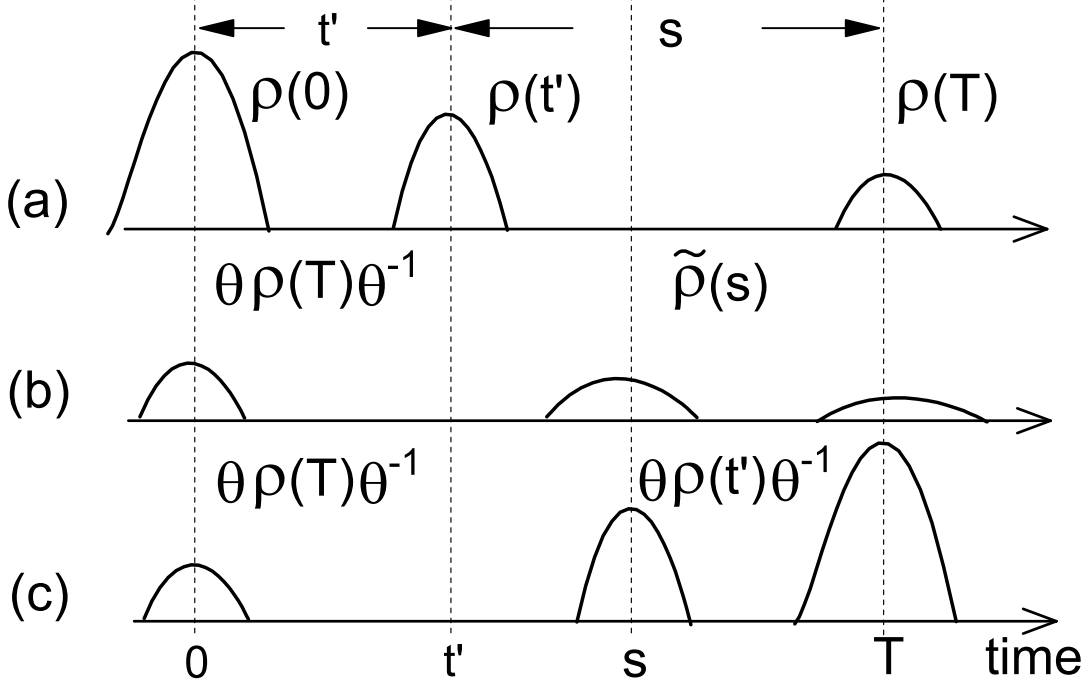


FIG. 1: (a) An irreversible time process of the system L_t . (b) The real time process of the time-reversal system \tilde{L}_s with a specified initial condition $\Theta\rho(T)\Theta^{-1}$. (c) The imaginary process constructed by the time reversed operator $\Theta\rho(t')\Theta^{-1}$, which is usually inconsistent with $\tilde{\rho}(s)$ due to dissipation.

where A denotes an arbitrary operator, $t'=T-s$ is the backward time [30], Θ is time-reversal operator and we use a new time parameter s ($0 \leq s \leq T$) for the time-reversal system. Specifically, if the system is consistent with its time-reversal, we call such a kind of system to be symmetric or invariable under time-reversal. These definitions are in fact a simple quantum extension of those in classical Markovian process [31, 32].

Operator $R(t', T)$ If the dissipation term L_t^{irr} vanishes, and the Hamiltonian H_t is even under the time reversal, namely, $H_s = \Theta H_{t'} \Theta^{-1}$, one may easily prove that a time-reversed operator, $\Theta\rho(t')\Theta^{-1}$, is the solution of the time-reversal system (4) with a specified initial condition $\Theta\rho(T)\Theta^{-1}$. We call such kind of solution to be time-reversible. In addition, if the system is symmetric under time-reversal and is at thermal equilibrium state ρ_0 , the state is also time-reversible and invariable specifically, i.e., $\Theta\rho_0\Theta^{-1} = \rho_0$. Generally speaking, as open quantum system has a dissipative term, if it is perturbed by time-dependent sources, and/or is relaxing to its equilibrium state, the solution $\rho(t)$ is no longer reversible. This observation could be simply quantified if we introduce an operator $R(t', T)$ satisfying a relationship of

$$\tilde{\rho}(s) = \Theta R(t', T) \rho(t') \Theta^{-1}, \quad (7)$$

and $R(T, T) = 1$. Obviously, if the solution $\rho(t)$ was reversible, $R(t', T)$ would equal the identity operator during the whole time interval; otherwise it would not. Fig. 1 schematically explains the reason which we define the operator $R(t', T)$.

Substituting (7) into Eq. (1), we can obtain an equation of motion for $R(T, t')$ with respect to the backward time t' given by

$$\begin{aligned} \partial_{t'} R(t', T) &= -L_{t'}^* R(t', T) - R(t', T) [\partial_{t'} \rho(t') - L_{t'} \rho(t')] \rho(t')^{-1} \\ &\quad - \left\{ \sum_j [R(t', T) V_j \rho(t'), V_j^\dagger] - [R(t', T) \rho(t') V_j^\dagger, V_j] \right\} \rho(t')^{-1} \\ &= -L_{t'}^* R(t', T) - \mathcal{O}_{t'} R(t', T), \end{aligned} \quad (8)$$

where the adjoint generator is $L_t^* A = i[H_t, A] + (1/2) \sum_j [V_j^\dagger, A] V_j + V_j^\dagger [A, V_j]$ and $L_t^* 1 = 0$ particularly. In the remaining part, we use the superscript $(\dots)^*$ to denote an adjoint super-operator with respect to the trace unless otherwise stated. Notice that this is a terminal condition problem instead of conventional initial condition problem. If we regard the term having the super-operator \mathcal{O}_t in Eq. (8) as a perturbation, which is rational because we concern about the deviation of $R(t', T)$ with respect to 1, we can obtain a formal solution for $R(t', T)$ using the Dyson series [23, 24]:

$$R(t', T) = [G^*(t', T) + \sum_{n=1}^{\infty} \int_{t'}^T dt_1 \cdots \int_{t_{n-1}}^T dt_n \prod_{i=1}^n G^*(t_{i-1}, t_i) \mathcal{O}_{t_i} G^*(t_n, T)] R(T, T) \quad (9)$$

where $G^*(t', T) = \mathcal{T}_+ \exp[\int_{t'}^T d\tau L_\tau^*]$ is the adjoint propagator of the system, and \mathcal{T}_+ denotes the antichronological time-ordering operator [29].

operator equality on the entropy production. Although we have the formal expression for $R(t', T)$, it is not satisfied because the perturbation in Eq. (9) involves $\rho(t')$, which makes its physical explanation ambiguous. In order to proceed further, in this work we restrict the system to those satisfying instant detailed balance condition with respect to their instant thermal equilibrium state $\rho_0(t)$ [33, 34]:

$$L_t^{\text{rev}} \rho_0(t) = 0, \quad (10)$$

$$L_t^{\text{irr}} A \rho_0(t) = L_t^{\text{irr}*} [A] \rho_0(t). \quad (11)$$

These conditions mean that the system always relaxes to its thermal equilibrium state $\rho_0(t)$, if the external source is fixed at the value with time point t [35]. This limitation seems not very strict from physical point of view. Under this circumstance, we may define an auxiliary operator $R_0(t', T)$ as follows:

$$R(t', T) \rho(t') = R_0(t', T) \rho_0(t'). \quad (12)$$

One can prove that the equation of motion for $R_0(t', T)$ is analogous to Eq. (8) except that the previous perturbation term is now replaced with

$$-\mathcal{W}_t R_0(t', T) = -R_0(t', T) \partial_{t'} \rho_0(t') \rho_0(t')^{-1}, \quad (13)$$

and the terminal condition of $R_0(t', T)$ is $\rho(T) \rho_0^{-1}(T)$. The reader is reminded that the new defined \mathcal{W}_t is a super-operator, though its action on an operator is a simple multiplication from the operator's right-hand side.

As we mentioned previously, a deviation of $R(t', T)$ with respect to 1 indicates the time-irreversibility of the solution $\rho(t)$. Hence, selecting $t'=0$, regarding the logarithms of the all density operators as “small” operator and using the relation (13) and the Dyson series for $R_0(0, T)$, we can expand $R(0, T)$ around 1 until the first order:

$$R(0, T) = 1 + \Theta^{-1} \ln \tilde{\rho}(T) \Theta - \ln \rho(0) + \cdots \quad (14)$$

$$= 1 + G^*(0, T) \ln \rho(T) - G^*(0, T) \ln \rho_0(T) + \int_0^T d\tau G^*(0, \tau) \partial_\tau \ln \rho_0(\tau) + \ln \rho_0(0) - \ln \rho(0) + \cdots \quad (15)$$

The first equation arises from the definition (7), and in the latter equation we have used a simple property of $G^*(0, T) 1 = 1$. We must point out explicitly that the first order expansion has also been applied to the super-operator \mathcal{W}_τ . Notice that the above equation also holds if the initial time 0 is replaced with arbitrary time point $t' (\leq T)$.

We find that an equal of Eqs. (14) and (15) provides us an microscopic expression for the second law of thermodynamics. To see it, Multiplying them with $\rho(0)$ and taking the trace, we have

$$\begin{aligned} & \langle \ln \rho(0) \rangle_0 - \langle \Theta^{-1} \ln \tilde{\rho}(T) \Theta \rangle_0 \\ &= [-\langle \ln \rho(T) \rangle_T + \langle \ln \rho(0) \rangle_0] + [\langle \ln \rho_0(T) \rangle_T - \langle \ln \rho_0(0) \rangle_0 - \int_0^T d\tau \langle \partial_\tau \ln \rho_0(\tau) \rangle_\tau] \end{aligned} \quad (16)$$

where $\langle A \rangle_\tau = \text{Tr}[A \rho(\tau)]$, we have used properties of $\text{Tr}[G^*(t', T)(A)B] = \text{Tr}[AG(T, t')(B)]$ and $G(\tau, 0)\rho(0) = \rho(\tau)$. Here $G(T, t')$ is the system's propagator and equals $\mathcal{T}_- \exp[\int_{t'}^T d\tau L_\tau]$, and \mathcal{T}_- is the chronological time-ordering operator [29]. We see that, on the right-hand side of Eq. (16), the terms in the first square bracket is the change of von Neumann entropy of the system, $S(\rho(\tau)) = -\langle \ln \rho(\tau) \rangle_\tau$, while the terms in second square bracket is the mean heat transfer from the system to the heat reservoir. The latter is consequence of the first law of thermodynamics [25], which becomes obvious if the quantum master equation is obtained under the weak coupling limits and the equilibrium state $\rho_0(t)$

has a canonical ensemble [26, 36, 37]. According to the principles of phenomenological thermodynamics [1], the whole expression on the right-hand side is no other than the mean entropy production of the irreversible quantum process and it is always assumed to be nonnegative. Deffer and Lutz obtained the same expression by the principle directly [22]. Compared with their argument, here two interesting features are revealed by the terms on the left-hand side of Eq. (16). First, because of the equal between two sides, we have a new form for the mean entropy production, which is based on the initial and terminal density operators of the original and time-reversal systems, respectively. In particular, if the initial state is time-reversal invariable, e.g., the system initially being a thermal equilibrium, the expression of left-hand side is just a quantum relative entropy, $S(\rho(0)||\tilde{\rho}(T))$ [38]. Under this circumstance, the nonnegative property of the mean entropy production has a rigors mathematical foundation rather than phenomenological reason. Second, if we concerned about a relaxation process of a time-reversal symmetric system from nonequilibrium initial state $\rho(0)$ to the thermal equilibrium ρ_0 after time T without any external perturbation [35], the expression on the left-hand side would become $S(\rho(0)||\rho_0)$. The reason is that the time-reversal system starts from the equilibrium initial state ρ_0 that is also the terminal state of the relaxation process. Therefor, $\tilde{\rho}(T)$ would equal ρ_0 . In this case, the equal between two sides of Eq. (16) becomes trivial.

Now we present an operator equality on the entropy production:

$$1 = \langle \rho(T) \rho_0(T)^{-1} \mathcal{T}_- \exp[\int_0^T d\tau \partial_\tau \rho_0(\tau) \rho_0^{-1}(\tau)] \rho_0(0) \rho^{-1}(0) \rangle \quad (17)$$

Proof:

$$\begin{aligned} 1 &= \text{Tr}[\Theta^{-1} \tilde{\rho}(T) \Theta] = \text{Tr}[R_0(0, T) \rho_0(0)] \\ &= \text{Tr}\{[G^*(0, T) + \sum_{n=1}^{\infty} \int_{t'}^T dt_1 \cdots \int_{t_{n-1}}^T dt_n \prod_{i=1}^n G^*(t_{i-1}, t_i) \mathcal{W}_{t_i} G^*(t_n, T)] [\rho(T) \rho_0^{-1}(T)] \rho_0(0)\} \\ &= \text{Tr}[\rho(T) \rho_0^{-1}(T) G(T, 0) \rho_0(0)] + \int_0^T dt_1 \text{Tr}[\rho(T) \rho_0^{-1}(T) G(T, t_1) \partial_{t_1} \rho_0(t_1) \rho_0^{-1}(t_1) G(t_1, 0) \rho_0(0)] + \cdots \\ &= \langle \rho(T) \rho_0(T)^{-1} \rho_0(0) \rho^{-1}(0) \rangle + \int_0^T dt_1 \langle \rho(T) \rho_0(T)^{-1} \partial_{t_1} \rho_0(t_1) \rho_0^{-1}(t_1) \rho_0(0) \rho^{-1}(0) \rangle + \cdots \end{aligned}$$

The transformation from the third line to the forth line is based on the definition of multi-time correlation for operators in quantum master equations [23, 39]. We must emphasize that, expanding the time-ordered exponential term in the operator equality to the first order does not simply lead into the mean entropy production equation (16), since $\partial_\tau \rho_0(\tau) \rho_0^{-1}(\tau)$ usually does not equal $\partial_\tau \ln \rho_0(\tau)$, which is unique only in quantum physics.

Quantum Jarzynski equality Chetrite and Mallick have derived an operator Jarzynski equality using a modified dynamics for the accompanying density matrix [23]. Here we can give an alternative derivation using the same sprint deriving Eqs. (17). Following the conventions of proving Jarzynski equality [9, 10, 23], we assume that the system has instant equilibrium solutions $\rho_0(t)$ satisfying the detailed balance condition, and the system is initially in equilibrium of $\rho_0(0)$. Analogous to previous case, we are still interested in comparing two processes from the original system and the time-reversal system using (7), but here the initial density operator of the latter process is replaced with $\tilde{\rho}(0) = \rho_0(T)$. Therefor, the terminal condition $R(T, T)$ becomes $\rho_0(T) \rho^{-1}(T)$ instead of previous 1. Because of the instant detailed balance condition, we may introduce an auxiliary $R_0(t', T)$ as (12) again and doing the same calculation to obtain the operator Jarzynski equality

$$1 = \langle \mathcal{T}_- \exp[\int_0^T d\tau \partial_\tau \rho_0(\tau) \rho_0^{-1}(\tau)] \rangle_0 \quad (18)$$

Here the subscript 0 is to indicate that the equality holds only for equilibrium initial condition. Obviously the operator equalities (17) and (18) are not the same unless both the initial and terminal states of the nonequilibrium process are thermal equilibriums.

Discussion and conclusion By investigating the difference between the density operators of quantum Markovian master equation and its time-reversal, in this work we present an operator equality on the entropy production. Our discussion is based on there key assumptions. The first two assumptions are a description of perturbed quantum system using the Markovian master equation and the system satisfying instant detailed balance condition, respectively. Although the two assumptions seem to limit the validity of the operator equality in very far from

equilibrium regime, we should emphasize that analogous assumptions in fact have been implied in derivation of the various fluctuation relations in classical Markovian systems. The last assumption is the existence of $\ln \rho(t)$, or equivalently the system's density operator to be invertible. So far, we do not find a satisfying mathematical or physical approach to justify it. Hence, we have to leave it for future study. Finally, we may point out that an extension of present theory to the classical Markovian processes is very straightforward.

We appreciate Prof. Chetrite for sending their inspiring work [23] to us. This work was supported by the National Science Foundation of China under Grant No. 11174025.

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